methanol solvent could cause some inactivation of the acrylic acid, thereby depleting the effective polymerization concentration of this monomer.

The feed ratio of the copolymerization affects the incorporation of SO_2 into the copolymer very slightly. For a feed ratio variation factor of 5, the copolymer composition increased by a factor of 1.4 with respect to SO_2 (*Table 4*). We suggest that the copolymerization reaction between acrylic acid and sulphur dioxide is somewhat different from the vinylic copolymerization reaction.

To test whether any adverse side reactions may be complicating the copolymerization, the components in a solution polymerization were mixed in various sequences. The results indicate that sequence has no influence essentially on SO_2 incorporation.

A more detailed investigation must be carried out to obtain a better understanding of this system. Studies are continuing.

Acknowledgement

The support of Inco Ltd. in various aspects of this study is greatly appreciated.

References

1 Dainton, F. S. and Ivin, K. J. *Quart. Rev.* 1958, **12**, 61
2 Ivin, K. J. and Rose, J. B. *Adv. Macromol. Chem.* 1968, **1**, 335
3 Tokura, N. *Encyclopedia of Polymer Science and Technology* 1968, **9**, 460
4 Tsuruta, T. and O'Driscoll, K. F. 'Structure and mechanism in vinyl polymerization, Marcel Dekker Inc., N. Y. 1969, p 91
5 Ryder, L. L. and Marvel, C. S. *J. Am. Chem. Soc.* 1935, **57**, 2311
6 Ryder, L. L. and Glavis, F. J. *J. Am. Chem. Soc.* 1937, **59**, 1014
7 Tokura, N., Matsuda, M. and Yazaki, F. *Makromol. Chem.* 1960, **42**, 108
8 Ghosh, P. and O'Driscoll, K. F. *J. Macromol. Sci. Chem.* 1967, **1**, 1393
9 Frith Jr, W. C. and Palmer, L. E. *Macromolecules* 1971, **4**, 654
10 Cais, R. E. and Stuk, G. J. *Polymer* 1978, **19**, 179
11 Mazzolini, C., Patron, L., Moretti, A. and Campanelli, M. *Ind. Eng. Chem., Prod. Res. Dev.* 1970, **9**, 504
12 Oster, B. and Lenz, R. W. *J. Polym. Sci., Chem.* 1977, **15**, 2479
13 Schneider, C., Denaxas, T. and Hummel, D. *J. Polym. Sci. C*, 1967, **16**, 2203

Preparation and application of functional polymers. Preparation of carbodiimides, ketenimines and imidoyl bromides using a poly(styryl diphenylphosphine dibromide)

Ahmed Akelah and Mohamed El-Borai
Department of Chemistry, Faculty of Science, Tanta University, Tanta, Egypt

(Received 12 October 1979; revised 6 December 1979)

The utilization of insoluble functionalized polymers was first developed by Merrifield for polypeptide synthesis[1]. After the successful application of solid phase peptide synthesis was reported, the synthesis and utilization of insoluble functionalized polymers as reagents and catalysts in other organic synthesis wide application[2–4].

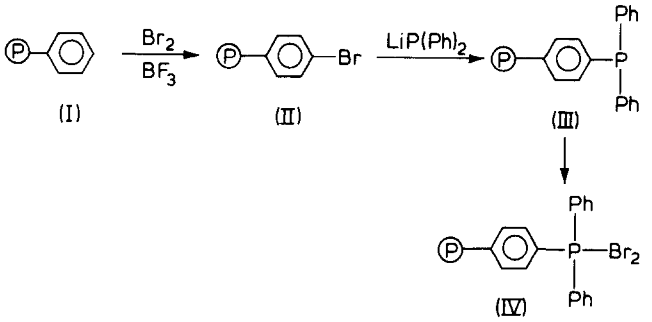
Because of the advantages of using insoluble resins, polymer-supported organophosphorous reagents were used recently in the preparation of polymeric Wittig reagents[5–8]. Treating cross-linked polymeric triarylphosphines with alkyl halides gave polymeric phosphonium salts which, after treatment with strong base, reacted with carbonyl compounds to form various olefins. The olefins were separated from the cross-linked polymeric triarylphosphine oxide by simple filtration, thus removing the main problem of Wittig reactions.

However, polymeric trisubstituted phosphines were also used in the preparation of various transition metal catalysts[9–12] and in the preparation of polymeric trisubstituted phosphine dihalides[13,14]. Moreover, the polymeric triarylphosphine–carbon tetrachloride system was used as a mild and efficient reagent for conversion of alcohols or carboxylic acids to the corresponding alkyl chlorides or acid chlorides[15–18]. This technique removes the difficulty of separation by column chromatography which is not possible with acid chlorides. In addition, since the conditions are essentially neutral i.e. no HCl is evolved, the system is convenient for substrates which are sensitive to the presence of HCl.

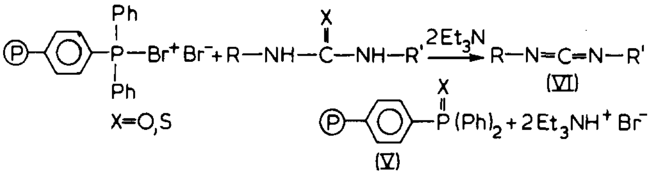
In this communication, we report the synthesis and successful application of 2% cross-linked poly(styryl diphenylphosphine dibromide) (IV) for the preparation of carbodiimides, ketenimines and imidoyl bromides.

Polymeric phosphine resin (III) was prepared by brominating 2% cross-linked polystyrene (I), then treating the brominated product (II) with lithium diphenylphosphine[13]. The resulting polymeric phosphine resins (III) were treated with bromine to give the polymeric reagent (IV):

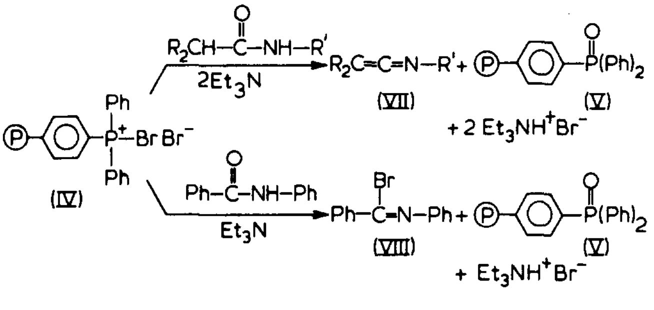
0032–3861/80/030255–03$02.00
© 1980 IPC Business Press



Treatment of polymeric phosphine dibromide resins (IV) with N,N′-disubstituted urea and thiourea in the presence of a base e.g. triethylamine, gave the corresponding carbodiimide, which was easily separated from the polymeric by-product (V) by simple filtration. Some carbodiimides prepared by using the polymeric reagent (IV) are summarized in *Table 1*.



Similarly, treatment of the resin (IV) with N,N′-disubstituted amides containing α–H gave ketenimines, as illustrated in *Table 2*.



Moreover, on treating the dibromide resin (IV) with N-phenyl-benzamide, which contains no α-H, N-phenylbenzimidoyl bromide (VIII) was synthesized.

In addition to the advantages of this polymeric reagent (easy separation of products by simple filtration, purity of products and mildness of reaction), the recovered polymeric phosphine oxide (V) is reconverted to the reactive polymer (III) by reduction with trichlorosilane[8,14,17] and reused in further applications. (We have used recovered resins (IV) in the conversion of diphenylurea to diphenylcarbodiimide (VIa) with 81% yield. This indicates that the reagent has lost some of its activity).

Experimental

General. N.m.r. spectra were recorded on a Bruker WH 90 spectrometer, and mass spectra on a AEJ-MS 50-DS 50 mass spectrometry unit.

The 2% cross-linked polystyrene resins were washed with 1N HCl, 1N NaOH, H_2O, methanol and ether, and dried, in order to remove surface impurities. Chlorodiphenylphosphine and solvents were distilled before use.

Preparation of poly(styryl diphenylphosphine dibromide) Poly(bromostyrene) (II). 100 g (0.63 mol) of bromine were added dropwise, in the dark, to a stirred mixture of 52 g (0.5 mol) of a washed 2% cross-linked polystyrene (I) and 34 g (0.5 mol) of BF_3 in 300 ml carbon tetrachloride, at a rate such that the reaction temperature did not exceed 25°C. After the complete addition of bromine, the mixture was stirred for 20 h at room temperature. The brominated beads were filtered, washed with CCl_4, acetone, and then with benzene until no brown filtrate was obtained. The yield of the dried resins was 92.5 g (anal. found: Br, 41.5).

Poly(styryl diphenylphosphine) (III). Lithium metal (3.5 g; 0.5 mol) was added to a solution of 25 g (0.11 mol) chlorodiphenylphosphine in 300 ml tetrahydrofuran under a stream of nitrogen. The mixture was stirred for 5 h at reflux temperature and then the excess pieces of lithium were carefully removed under nitrogen. 18.5 g (0.1 mol) poly(bromostyrene) (II) were added to this mixture under a nitrogen stream and the system was stirred at room temperature for 3 h. After stirring for 2 h at reflux temperature, the reaction mixture was cooled, hydrolysed with methanol–water and filtered. The filtered beads were washed with water, methanol, benzene and methylene chloride and dried *in vacuo* to give 25 g of resin (III).

Poly(styryl diphenyl phosphine dibromide) (IV). 24 g (0.15 mol) bromine were added dropwise under external cooling, (0–5°C) to a stirred suspension of 29 g (0.1 mol) poly(styryl diphenyl phosphine) (III) in 200 ml benzene. The mixture was stirred for 6 h at room temperature, filtered and then washed with benzene. The dried resins gave 44 g of (IV).

General procedure for preparation of carbodiimides. Triethylamine (10 g; 0.1 mol) was added dropwise to a stirred suspension of 22.5 g (0.05 mol) poly(styryl diphenyl

Table 1 Carbodiimides, R–N=C=N–R′, from urea and thiourea derivatives, R–NH–C=X·NH–R′

Compound	X	R	R′	Yield (%)	Boiling point
(VIa)	O	Ph	Ph	92	180–183°C/10 mm
	S	Ph	Ph	88	(ref. 7:163–165°C/11 mm)
(VIb)	O	Ph	C_6H_{11}	85	167–169°C/10 mm (ref. 7: 169–172°C/13 mm)
(VIc)	O	C_6H_{11}	C_6H_{11}	76	154–155°C/10 mm (ref. 7:158–160°C/12 mm)

Table 2 Ketenimines, R_2C=C=N–R′, from amides, R_2CH–C=O R_2CH–C=O·NH–R′

Compound	R	R′	Yield (%)	Temperature data
(VIIa)	Ph	Ph	90	M.p. 55–56°C (ref. 8:54–56°C)
(VIIb)	Me	Ph	70	B.p. 95–96°C/10 mm: (ref. 8:98–100°C/12 mm)
(VIIc)	Ph	n-Bu	89	B.p. 120–122°C/0.05 mm (ref. 9:137–138°C/0.1 mm)

phosphine dibromide) (IV) in 200 ml benzene. The reaction mixture was stirred for 1 h at room temperature and a urea (or thiourea) derivative (0.05 mol) was added in small portions. The system was refluxed for 2 h, cooled to room temperature and then filtered. The resins were washed with benzene and the combined filtrate was concentrated to give the corresponding carbodiimide (VIa–c; see *Table 1*). The carbodiimides were identified by ^{1}H n.m.r. and i.r. spectroscopy, and their boiling points.

General procedure for preparation of ketenimines. A mixture of 22.5 g (0.05 mol) (IV) and 10.1 g (0.1 mol) triethylamine in 200 ml benzene was stirred at room temperature for 30 min and then 0.5 mol of N-monosubstituted amide derivative in 100 ml benzene was added dropwise at room temperature. After complete addition, the system was refluxed with stirring for 2 h and the product filtered off. By-product resins were washed with ether, and the combined filtrate was distilled to give the ketenimine (VIIa–c, *Table 2*).

Preparation of N-phenylbenzimidoyl bromide. N-phenylbenzamide (9.85 g, 0.05 mol) was added to a stirred mixture of 22.5 g (0.05 mol) (IV) and 5 g (0.05 mol) triethylamine in 200 ml benzene. The reaction mixture was stirred for 5 h and filtered. The polymeric beads were washed with ether. The combined filtrate was concentrated and the residue was recrystallized to give 11.5 g (88%) of N-phenylbenzimidoyl bromide (VIII) with m.p. 40°C (ref. 22): m.p. 40–42°C, b.p. 150–160°C/0.005 mm).

Regeneration of poly(styryl diphenyl phosphine) (III). A solution of trichlorosilane (7.5 g; 0.055 mol) in 50 ml benzene was added to a stirred suspension of 15.2 g (0.05 mol) poly(styryl diphenyl phosphine oxide) (V) in 50 ml benzene. 6 g (0.055 mol) triethylamine were added to this mixture and the system was stirred for 10 h under reflux. The beads were filtered and washed successively with benzene and tetrahydrofuran. The resins were then treated with concentrated NaOH and washed. The dried resins were treated with bromine and reused in the same reactions.

References

1 Merrifield, R. B. *J. Am. Chem. Soc.* 1963, **85**, 2149
2 Leznoff, C. C. *Chem. Soc. Rev.* 1974, **3**, 65
3 Patchornik, A. and Kraus, M. A. *Pure Appl. Chem.* 1975, **43**, 503
4 Akelah, A., El-Borai, M. and Omara, M. A. to be published
5 Camps, F., Castells, J., Font, J. and Vela, F. *Tetr. Lett.* 1971, 1715
6 Heitz, W. and Michels, R. *Angew. Chem.* 1972, **84**, 296
7 McKinley, S. V. and Rakshys, J. W. *J. Chem. Soc. Chem. Comm.* 1972, 134
8 Heitz, W. and Michels, R. *Leibigs Ann. Chem.* 1973, 227
9 Bailar, J. C. *Catal. Rev.* 1974, **10**, 17
10 Haag, W. and Whitehurst, D. D., 'Catalysis', Vol 1, North Holland, New York, 1973, p 29
11 Grubbs, R. H., Sweet, E. M. and Phisanbut, S. 'Catalysis in Organic Synthesis', (Eds. P. N. Rylander and H. Greenfield) Academic Press, 1976, p 153
12 Pittman, C. U., Jacobson, S., Smith, L. R., Clements, W. and Hiramoto, H. 'Catalysis in Organic Synthesis' (Eds. P. N. Rylander and H. Greenfield) Academic Press, 1976, p 161
13 Relles, H. M. and Schluenz, R. W. *J. Am. Chem. Soc.* 1974, **96**, 6469
14 Michels, R. and Heitz, W. *Makromol. Chem.* 1975, **176**, 245
15 Appel, R. and Willms, L. *J. Chem. Res.* 1977, 84
16 Hodge, P. and Richardson, G. *J. Chem. Soc. Chem. Comm.* 1975, 622
17 Regan, S. L. and Lee, D. P. *J. Org. Chem.* 1975, **40**, 1669
18 Harrison, C. R., Hodge, P. and Rogers, W. J. *Synthesis* 1977, 41
19 Schlack, P. and Keil, G. *Liebigs Ann. Chem.* 1963, **661**, 164
20 Staudinger, H. and Hauser, E. *Helv. Chim. Acta* 1921, **4**, 887
21 Stevens, C. L. and French, J. C. *J. Am. Chem. Soc.* 1954, **76**, 4398
22 Zbiral, E. and Bauer, E. *Phosphorus* 1972, **2**, 35